SENSORS FOR CARBONIZATION CONTROL

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INTRODUCTION

Phase I of "Research on Intelligent Processing of Carbon-Carbon Composites" is a two year program to develop enabling technologies for real time control of the carbonization process for resin matrix composites. The research has three related foci: *in situ* material property sensors; process models; and intelligent control architecture. The research has, to date, 1) developed control strategies at three levels of sophistication that use sensors and models to complete carbonization more rapidly while still reducing losses; 2) developed a control architecture that integrates those sensors and models; 3) conducted successful *in situ* tests of chemical and physical property sensors; 4) developed a high temperature eddy current sensor (not yet tested *in situ*); 5) developed considerable kinetic data on the carbonization reactions, described the basic reaction paths and their relation to physical properties qualitatively, and developed a kinetic equation for the lowest temperature family of carbonization reactions, the production of water from hydroxyl groups; 6) defined the modeling strategy for calculating gas pressure and the experimental strategy for developing models for matrix strength. In the following, we describe the general problem and the issues in modeling and control to provide a context for the sensor results.

The most important problem in manufacture of carbon carbon composites is the loss to delamination of components during first carbonization. Stresses are produced by internal gas production, thermal expansion and contraction, and matrix chemical contraction. The matrix permeability to gases is changing, and its strength is also changing. Thus, preventing delamination from gas pressure (thought to be the primary problem) entails predicting the rate gas will be produced, predicting the rate at which it will escape (to calculate the pressure), predicting the strength, and then applying a failure criterion. One expects the strength to change fairly smoothly during the process, so that relating careful experimental measurements to the matrix state should make prediction from material state possible. The key control modeling issue, therefore, is the calculation of gas pressure, which entails the rate of production and the rate of escape, and the effective use of sensors to improve such predictions in real time.

In the following we first give a brief description of the control strategy and control architecture results to provide a context for the modeling and sensor results to follow. Three control strategies will actually be described. The Phase I control architecture implements the Level 0 strategy in a testbed to interpret real time data and to identify weak links in the models. The testbed controller is expected to be substantially faster and more reliable than current manufacturing practice, and to be extensible with better models and sensors in the future.

CONTROL STRATEGY

Extensive discussion with process experts established that the primary control system goal should be to complete the carbonization process as rapidly as possible while keeping the risk of delamination low. This is a goal (to complete the process) and a constraint (acceptable risk). That goal can be broken into subgoals: 1) remove by heating (nearly all) non-carbon elements of the matrix *and* restore matrix strength by further heating (the strength first decreases and then increases), and 2) cool to near room temperature.

The Level-1 IPM control strategy can be most easily grasped with the conceptual aid of idealized sensors. If we had a "completion of carbonization" sensor, a "strength" sensor, a "risk-of-failure" sensor, and heating and cooling mechanisms that allowed very rapid change of material temperature, these goals could be achieved by a fairly simple strategy. The system would start heating the component slowly (because rapid changes in heating rate create non-uniform temperatures that increase risk and may do irreversible damage) and increase the heating rate until either the heater's limit was reached or the risk of failure rose to the limit (say 4%), then adjust the heating rate to keep the risk of failure constant until the desired strength and carbonization states were reached. It would then begin to cool slowly and then more rapidly until the risk of failure limit or the cooling capacity limit was reached. This simple strategy can be refined (our Level-2) to achieve higher speed and better final properties, but let us first examine how it can be implemented.

The Level-1 carbon-carbon IPM control system approaches this ideal strategy by inferring the risk of failure using models, multiple sensors, and heuristic knowledge. It compensates for unavoidable thermal lag by predicting the future risk of failure and planning its future control actions. That is, instead of setting temperature or heating rate based on present sensor data, it projects that data a modest distance into the future, estimates from it the safety index (defined below), and resets the future temperature and heating rate.

There are two critical issues: 1) can we avoid delamination if we know the risk of failure is significant? and, 2) can the system actually infer something like a risk of failure from a combination of real sensors, models and heuristics? The answer to the first is that we certainly can in many cases. Process-induced delaminations originate from continuously changing values of gas pressure, chemical change induced shrinkage, temperature (thermal stress), modulus and matrix strength. Since reaction rates are directly and strongly influenced by temperature, and these, in turn, determine gas evolution, intelligent control of temperature and the rate of change of temperature can control the risk of delamination due to gas pressure or thermal stresses. The effect of processing on total shrinkage and net strength is not thought to be very large, although the rate is certainly controllable. That dependence on rate will be used to improve process reliability. The answer to the second question is also a qualified "yes". The combination of models and sensors to provide a "risk-of-failure" sensor is described below.

Probability and Safety

We denote by $F_{strength}(\sigma)$ the probability that the strength of the composite is less than σ, and by $p(\sigma)$ the probability that the peak stress is between σ and $\sigma + d\sigma$, related to a probability density $f_{stress}(\sigma)$ by $p(\sigma) = f_{stress}(\sigma)d\sigma$. The probability of failure p_F is related to the overlap of the stress and strength probability distributions, and is given by

$$p_F(t) = \int_0^\infty f_{stress}(t, \sigma)F_{strength}(t, \sigma)d\sigma \qquad (1)$$

Both distributions change significantly during the process, and the system must have some knowledge of each.

The similarity of the risk issues to those encountered in structural design suggests simplifications. Engineering design practice deals with uncertain strength and variable loads

by designing so that the maximum stress σ_{max} is less than some fraction 1/n of the nominal (expected or average) strength S,

$$\sigma_{max} \leq S/n \ . \tag{2}$$

The number n is called the *safety factor*. Some simple probability analyses can show that, since existing carbonization practices succeed most of the time in spite of substantial variability in stresses and strengths, the effective safety factor is now much greater than 1 during most of the process. This excess safety factor offers the opportunity for considerable economies. A somewhat more sophisticated approach, also borrowed from engineering design practice, uses the *safety index*, defined by

$$\beta = \frac{\langle (S - \sigma_{max}) \rangle}{\sqrt{\left[\text{var } S + \text{var } \sigma_{max} \right]}} \tag{3}$$

The quantity in angle brackets is the expected or mean value of strength minus maximum stress. The denominator is the standard deviation of the numerator. The safety index is, thus, the expected value of the failure variable (strength minus stress) measured in units of its own standard deviation. A safety index of three means three standard deviations from failure. This is a more useful measure of risk than the safety factor because it recognizes that risk increases when the uncertainty is large even if the mean values don't change. It is much easier to obtain, however, than the actual probability of failure.

Risk-of-Failure Sensor

The Level-1 control strategy uses safety index as the measure of risk of failure. The matrix strength will be determined as a function of state by a series of fracture mechanics experiments at high temperature. The permeability will be determined similarly. The Level-1 intelligent controller will monitor thermal gradients, weight loss, and gas evolution, as well as other properties discussed below. From weight loss and gas evolution it will infer current state, and will predict future state and gas pressure from kinetic equations and the previously measured state-dependent permeability. From the stored strength and previously measured state-dependent strength values (and standard deviations), it will estimate the safety factor. The modeling and sensor sections describe the models in more detail.

The Level-2 control strategy uses a *set* of safety indices. That strategy uses a safety index $\beta_i(t, \mathbf{x})$ for each important failure mode, and the controlled variable is the minimum of this set over all locations. (Remember that a zero or negative safety index means predicted failure.) The Level 2 safety indices are calculated more accurately by using better models for the (state dependent) thermal transport, coefficient of thermal expansion and by better models for the matrix toughness and the flaw distribution. A more accurate safety index makes the controller automatically complete the process more rapidly, since uncertainty decreases the safety index (the denominator is larger), and the controller's efforts to keep it constant at a higher (safer) value results in slowing the process.

The Level-2 intelligent control system also exploits better models for the effect of processing on strength and permeability to make trade-offs between different stages of the process. That is, doing one stage of the reaction slower or faster may have considerable benefits at a later stage of the process. Such phenomena are real, but are often hard to recognize even with very good models. It entails answering "What is the best path?", rather than "How good is a particular path?". This is called the "inverse problem" in partial differential equations and decision theory, and is usually very difficult to solve rigorously. Expert rules, therefore, are likely to be useful in making these complex tradeoffs even at Level-2.

The Level-0 control strategy controls defines safety factors in terms of maximum allowed thermal gradient and maximum allowed gas pressure, rather than strength-stress. It controls the smallest of these safety *factors*, not safety *indices*, because of insufficient know-

ledge of the standard deviations. The system uses experiential limits on thermal gradients because of the absence of good models for the thermal expansion and thermal conductivity as they depend on matrix state and fiber and weave properties. Because of limited accuracy in the state-dependent strength and permeability models, the Level-0 system uses larger safety factors than might be necessary. If permeability knowledge is very inaccurate, this level controller will use experiential limits on gas evolution rate, dispensing with strength estimates entirely.

All three levels use, in addition to the sensors previously mentioned, acoustic emission and eddy current sensors. The acoustic emission sensors play two important roles: 1) The AE has been shown in this program to detect delamination, and that is a powerful tool to test and to improve models for failure; 2) AE is sensitive to microstructural development and to important physical state changes such as the transition from compressive (thermal expansion) to tensile (chemical shrinkage) stresses. The eddy current sensor is sensitive to the extent of matrix carbonization (more precisely, to its electrical conductivity at 1MHz). Both the acoustic emission and the eddy current measurements are potentially useful in updating models for matrix strength and permeability.

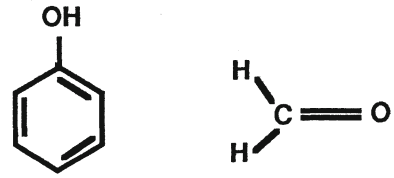
A concrete example of the use of the intelligent control testbed in carbonization experiments clarifies the system's function in materials science experiments. The laboratory detection of delaminations with acoustic emission (AE) is an important indicator of the potential value of AE in modifying the process to avoid future failures. The origin of the failure, however, has not yet been unambigously identified. Because of the temperature and time regime, it must have resulted from either thermal stresses or water evolution gas pressure. (The heating rate was very high (> 100°C/hr), and the failed specimen was non-uniformly reacted, so thermal stresses may have been the cause. On the other hand, the permeability was low at that stage, and rapid heating might have produced excessive internal pressure.)

That experiment (or a variant of it) will be repeated with the intelligent control system comparing predicted water production rates to observed water production rates to detect possibly large pressure buildup, and monitoring edge and center temperatures. It will also infer interior temperature from heat transport equations. When the IPM system recognizes the delamination, it will search the gas evolution rate measurements for a burst of gas at the time of the AE failure signal (not detected until several minutes later), compare the prior observed rate to the rate estimated from the model calculation. The Level-0 IPM system will also examine the thermal gradients for indications of excessive thermal strain, and search the previous acoustic data for indications of precursor strain relief.

In this situation, the IPM controller serves a diagnostic, interpretative function for the development of deeper knowledge for subsequent processing. That analysis is tedious for a scientist; its automation will make possible progress on deeper issues. It also is useful in bringing more materials science expertise and tools to the failure diagnosis than a single engineer may have available. The resulting understanding of the delamination can be employed by the controller itself for reducing failure risk and to improve failure models.

MODELS

The resin used in the program is a commercial phenol formaldehyde (Fiberite's K-641). This is a complex polymer obtained by condensation of phenol (Fig 1, I) and formaldehyde (Fig. 1, II).



Phenol **Formaldehyde**
I **II**

Fig. 1. Structure of phenol and formaldehyde used in the resin.

The repeating unit in the cured polymer consists of a methylene bridge (-CH_2-) and a hydroxyphenyl group (-C_6H_3OH-). Each aromatic ring has one hydroxyl substituent and is bonded to at least two methylene groups. The typical structure of the (cured) polymer is shown in Fig. 2. Occasionally a third methylene group is attached to the aromatic ring to start a branched chain, and the polymer is said to be crosslinked. The dominant products were found to be water (H_2O), methane (CH_4), hydrogen (H_2), carbon oxides (CO and CO_2) with small amounts of ethane (C_2H_6), propane (C_3H_8) (from the decomposition of isopropyl alcohol), toluene ($C_6H_5CH_3$), cresol ($CH_3C_6H_5OH$) and phenol (C_6H_5OH).

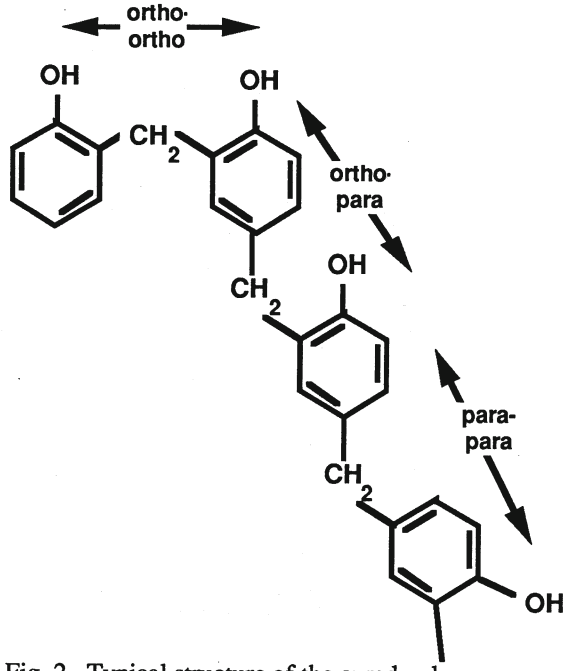


Fig. 2. Typical structure of the cured polymer.

The low temperature reactions (up to about 450°C) have been analyzed in some depth and a kinetic model developed. These entail[1] the formation of water from the hydroxyl (OH) groups, leaving an ether (-C-O-C-) bond in the matrix. The hydroxyl groups can be bonded to a ring carbon that is either adjacent (ortho) or opposite (para) to the ring carbon attached to the methylene bridge between rings. Possible combinations are shown in Fig. 2, above. Only adjacent ortho pairs react to form water.

The shrinkage vs. processing temperature, as measured at room temperature, is shown in Fig. 3. The results suggest strongly, that the water production reaction is the dominant source of matrix shrinkage. That makes control of shrinkage rate and concomitant stresses feasible.

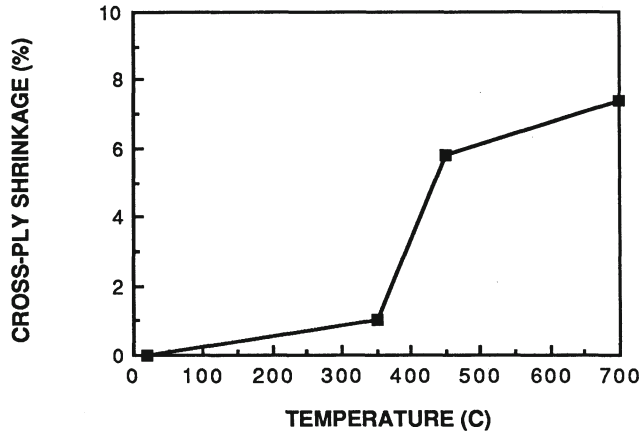


Fig. 3 Percentage through thickness shrinkage after return to room temperature vs. processing temperature.

The number of hydroxyl groups able to react increases with temperature, probably due simply to softening of the matrix and concomitant improved mobility. This family of reactions is found to be well summarized by the equations (due to Dr. Mark Cher, Rockwell)

$$\frac{d\pi_{OH}}{dt} = -k(T)\pi_{OH}^{\text{reactive}} \qquad (4)$$

$$= -k(T)\,[\pi_{OH} - \gamma(T)N\Omega/2]$$

where π_{OH} is the total number of hydroxyl pairs, $\pi_{OH}^{\text{reactive}}$ is the number of pairs that are reactive at temperature T, N is the number of monomer units, Ω is the fraction of monomers that are ortho-ortho pairs (a necessary condition for reaction), and $\gamma(T) = 1 - \beta(T)$ is the fraction of pairs that are thermally frozen at temperature T, and $\beta(T)$ is the mobile fraction. For isothermal experiments only, Eq. 4 can be integrated immediately to obtain

$$\pi_{OH}(t) = \frac{N}{2}[1 - \beta\Omega(1 - e^{-kt})] \qquad (5)$$

Eq. 4 can be integrated numerically for temperature/time dependence appropriate to the carbonization control process. The rate at which water is produced is the negative of the right side of Eq. 4. Eq. 4 predicts gas production (water) and weight loss (also water) fairly well from room temperature up to about 400° to 450°C, where other reactions involving the production of methane, carbon oxides and hydrogen become important.

Although phenomenological rate equations like Eq. 1 summarize many possible intermediate states, they are clearly related to identifiable products in the gas phase and in the matrix state. They are, therefore, a considerable advance over previous results that parametrized weight loss rates in terms of physically and chemically unknown weight loss components. Because those components were not identified, that state description could not be sensed[2] nor could the results be related in a fundamental way to other physical state variables such as the large changes in modulus and strength.

As temperature is increased above 400°C, a new family of reactions related to methylene bond cleavage to form methane were found. This family is conjectured to be the origin of the marked decrease in matrix modulus and strength found by other observers[3,4] in the region between about 450°C and 550°C. As temperature was increased still further, a new family of reactions apparently related to methylene bond reformation to produce an aromatic ring condensation and liberating hydrogen was discovered. This reaction family is the apparent origin of the modest increase in matrix strength and modulus observed by other workers in the regime between roughly 550°C and 700°C. Research continues on the development of phenomenological equations (analogous to Eq. 4, above) to summarize the rates of these reactions as a function of time and temperature.

These kinetic equations will make it possible to predict the rate of gas production within the composite. Those results, when combined with a transport model, enable us to predict gas pressure. The essential components of the transport model are the equation for conservation of mass:

$$\frac{\partial \rho_g}{\partial t} + \nabla \cdot J_g = p\text{-}a \tag{5}$$

where ρ_g is the gas density inside the composite, J_g is the gas flow rate vector, p is the production rate, and "a" is the absorption rate; Darcy's law for the gas flux J_g,

$$J_g = - \frac{\kappa \rho_g \nabla P}{\mu_g} \tag{6}$$

where κ is the permeability of the composite to the gas, P is the pressure and μ_g is the gas viscosity; and lastly, the gas law relating the density to the temperature and pressure:

$$\rho_g = \frac{M_g P}{RT} \tag{7}$$

where M_g is the molecular weight of the gas. These equations can be combined to obtain a non-linear differential equation for the pressure.

The boundary conditions on the pressure at the surface of the composite are that the gas flow J_g and the pressure are continuous. To solve the problem rigorously, we would develop similar gas transport models for the retort. A useful approximate model, however, can be based on the approximation that sets the pressure to be that of the retort .

The gas production rate must be obtained from a kinetic model, as described above. The high temperature permeability will be measured for various carbonization states.

The last major model component is the relation between chemical and physical state and mechanical properties and, especially, mechanical failure by delamination. The strength and stiffness of the decomposing polymer are known to change drastically during the process. We will measure toughness and strength at temperature at various degress of carbonization to provide a basis for modeling their relationship to chemical and physical state, and thus to process control actions.

A more complete model for mechanical integrity would include the effects of curvature, thickness, fiber and (state dependent) matrix modulus, and weave pattern. The roles of these variables will be generally identified by the experiments and modeling during the remainder of Phase I.

SENSORS

The sensors tested sucessfully *in situ* during the first year are acoustic emission from microstructural changes and delamination[5]; gas chromatographic analysis of gas composition, monitoring of gas flow at inlet and outlet, monitoring of trace oxygen, *in situ* monitoring of weight loss, differential thermal analysis to monitor heat absorption by the (endothermic) carbonization process, and thermocouple monitoring of temperature. The electrical conductivity of cured neat resin (no fibers) was monitored *in situ* during carbonization, and found to change by 10 orders of magnitude. Fiber conductivity makes this sensor very difficult to use on composites, however. Eddy current measurements at room temperature on samples at various levels of carbonization showed a reproducible relative sensitivity to carbonization state. An increase in effective (matrix plus fiber) 1MHz conductivity of about 20% was observed. An eddy current sensor has been fabricated for high temperature *in situ* use and will be tested soon.

The role of the sensors has been generally described in the description of the control strategies. The differential thermal analysis provides a rough instantaneous measure of reaction rate. The rate of production of the principal products, water, methane, carbon monoxide, carbon dioxide, and hydrogen, and the cumulative values of those gases allow us to infer approximate matrix state. The rate of production is important to inferring internal pressure. With adequate models, permeability and strength can be calculated from matrix state. Physical state can be constrained by the weight loss, eddy current, and cumulative gas evolution. Acoustic emission both detects actual failure and senses the microstructural changes that release stress and improve permeability, allowing higher reaction rates (gas production). Temperature determines both reaction rate and thermal strain, so (thermocouple) measurement of temperature at several points is of obvious value.

PLANS FOR THE REMAINDER OF PHASE I

The second year of Phase I will bring together models and sensors to extend our knowledge of the complex chemical and physical phenomena occurring during carbonization and their relationships. The control system nucleus will facilitate these tests, and the process of assembling that core will help to identify the materials research that would most improve process control. The focus will be on understanding the relationships between measurements, material process phenomena, and controllable variables. This testbed will be a unique facility for exploring carbonization phenomena. It will have *in situ* material property and process sensors (listed above), basic models for the chemical reactions, gas production and transport, and for the development of strength and permeability (and thus pressure). Experimental tests of these models will be more rapid and detailed because the combination of models and multiple sensors can often rule out one or more competing hypotheses, accelerating the formalization of carbonization knowledge.

The resulting Level-0 controller will not, of course, have a deep model of all the relevant phenomena. Its use as a testbed will help to identify which of the many possible component properties (such as weave, curvature, thickness, fiber modulus) whose detailed modeling or replacement by improved materials would most contribute to improved processing and final properties. The Level-0 controller will also constitute a core that could be adapted to improve factory productivity and reduce losses on the complex carbon-carbon components of next generation systems like the National Aerospace Plane and SABIR.

ACKNOWLEDGEMENT

Research supported by DARPA and the Office of Naval Research under contract N00014-87-C-0724.

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